

Indian Journal of Chemistry
Vol. 57A, November 2018, pp. 1344-1350

Kinetic studies on liquid phase transesterification of dimethyl malonate with benzyl alcohol over modified ceria as efficient solid acid catalysts

Venkatesh^{a,b,c} & S Z Mohamed Shamshuddin^{a,b,*}

^aChemistry Research Laboratory, HMS Institute of Technology, NH₄, Kyathsandra, Tumakuru, Karnataka, India.

^bResearch and Development Center, Bharathiar University, Coimbatore, India.

^cChannabasaveshwara Institute of Technology, Gubbi.

Email: mohamed.shamshuddin@gmail.com

Received 28 December 2017; revised and accepted 15 October 2018

Solid acids such as ceria, zirconia, ceria-zirconia, sulphated-ceria and sulphated-ceria-zirconia (SCZ) have been prepared by impregnation method and characterized by NH₃-TPD for surface acidity, powder XRD for crystallinity and IR spectroscopy for functionality. Liquid phase transesterification of benzyl alcohol (BA) with dimethyl malonate (DMM) has been carried out in presence of these solid acid catalysts. Dibenzylmalonate (DBM) has been obtained as a major transester product. Various parameters such as reaction time, weight of catalyst, molar ratio of reactants and reaction temperature have been varied to obtain highest transester yield. Highest transester yield (88%) was obtained in presence of SCZ catalyst at a molar ratio of DMM:BA = 1:5, reaction time of 3 h and a temperature of 140 °C. Kinetic experiments confirm that SCZ catalytic system was efficient and facile.

Keywords: Transesterification, Modified ceria, Dibenzylmalonate, Benzyl methyl malonate

Nanomaterials containing ceria are important in the field of material sciences and catalysis due to their redox property & oxygen storage capacity at low temperature by virtue of their capacity to oscillate between two oxidation states +3 and +4¹. In recent years much attention has been focused on the synthesis of ceria doped zirconia or zirconia doped ceria materials due to their unique properties compared to zirconia or ceria alone. Recently heterogeneous catalysts are more preferred because of their high activity, selectivity, reusability, ease of separation & no contamination. Incorporation of zirconia cation into ceria unit cell and vice versa changes the surface acid-base site. Zr⁺⁴ & Ce⁺⁴ ions act as Lewis acid sites, O²⁻ ions as Lewis base sites³. Transesterification is one of the important acid-catalyzed reactions with a wide range of industrial applications as well as usage in laboratories⁴. Conventionally, transesterification is carried out in the presence of liquid acid catalysts such as HCl, H₂SO₄, H₃PO₄, etc. In view of these disadvantages of liquid acid catalysts, solid acids are preferred. Solid acids such as metal oxides, cation exchange resins, zeolites and their modified forms have been successfully used as catalysts for many acid catalyzed organic transformations like

isomerization⁵, dehydration⁶, acylation⁷, oxidation⁸, transesterification⁹⁻¹² and esterification reaction¹³.

Malonate esters are used as intermediate compounds in the synthesis of various complex compounds, pharmaceuticals, fine chemicals, drugs, plasticizers, food preservatives and cosmetics. Because of their importance in industrial application, transesterification of malonic esters with higher alcohols is widely studied¹⁴.

In transesterification with *n*-butanol, 75.2% of diethyl malonate was converted in 24 h with a selectivity of 98.8% over Sn incorporated mesoporous silica molecular sieve SBA-15. Vijayasankar *et al.*, reported that amorphous mesoporous iron aluminophosphates exhibited better catalytic activity in the transesterification of diethyl malonate and benzyl alcohol with higher yield and selectivity. Total transester yield was found to be 79% over the prepared FeAlPs¹⁵. Si MCM-41 supported heteropolytungstic acid (HPWA) was reported as a promising catalyst for the production of transesters in chemical industries¹⁴. Swarnali Pathak and Dibakar Chandra Deka reported the transesterification of dimethyl malonate with a novel catalyst derived from *Musa balbisiana* colla and the yield was found to be 40% in 59 h¹⁶. Minchitha *et al.*, reported

transesterification of diethyl malonate with benzyl alcohol using sulphate modified carbon nano tubes, total transester yield was found to be 73%¹⁷. In view of the industrial importance of esters, herein the transesterification of benzyl alcohol with dimethyl malonate is carried out using solid acids such as CeO_2 , $\text{CeO}_2\text{-ZrO}_2$, $\text{SO}_4^{2-}/\text{CeO}_2$ and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ in their powder form. Among these solid acids, $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ was found to be an efficient catalyst due to its high acidic strength, easy separation, eco friendliness and low cost.

The goal of the present work is to synthesize dibenzyl malonate via transesterification using ceria based solid acid catalysts. These solid acid catalysts were prepared by impregnation method. The prepared catalysts were characterized by NH_3 -TPD, Powder XRD, and FT-IR for their surface acidity, crystallinity and functionality. Transesterification of dimethyl malonate (DMM) with benzyl alcohol (BA) was studied over these ceria based solid acid catalysts. The yield of total transester and percentage selectivity towards the desired product was optimized by varying reaction time, reaction temperature, weight of the catalyst and molar ratio of the reactants. Reactivation & reusability studies were also carried out. A kinetic study was conducted for transesterification reaction by utilizing the data obtained under optimized reaction conditions. Transesterification of benzyl alcohol with dimethyl malonate was carried using modified ceria as an efficient solid acid catalyst.

Materials and Methods

Zirconyl nitrate and ceric ammonium nitrate were supplied by Sigma Aldrich Ltd, India, Sulphuric acid was procured from SD Fine Chemicals Ltd, India,

The solid acids were prepared by wet impregnation method as follow.

Preparation of ceria (CeO_2): 5.0 g of ceric ammonium nitrate was mixed with a limited amount of deionized water. This mixture was made into a paste. The resulting paste was dried in an air oven at 120 °C for 12 h and calcined for 5 h at 550 °C.

Preparation of zirconia (ZrO_2): 5.0 g of zirconyl nitrate was mixed with a limited amount of deionized water. This mixture was made into a paste. The resulting paste was dried in an air oven at 120 °C for 12 h and calcined for 5 h at 550 °C.

Preparation of sulphated ceria ($\text{SO}_4^{2-}/\text{CeO}_2$): 5.0 g of uncalcined hydrated CeO_2 was taken in a china dish to which 2 mL of 6M H_2SO_4 was added and the

resulting mixture was made into a fine paste. The paste was dried at 120 °C for 12 h and calcined at 550 °C for 5 h.

Preparation of ceria-zirconia ($\text{CeO}_2\text{-ZrO}_2$) mixed oxide: 5.0 g of ceric ammonium nitrate and zirconyl nitrate were mixed with limited amount of deionized water. This mixture was made into a paste. The resulting paste was dried in an air oven at 120 °C for 12 h and calcined for 5 h at 550 °C.

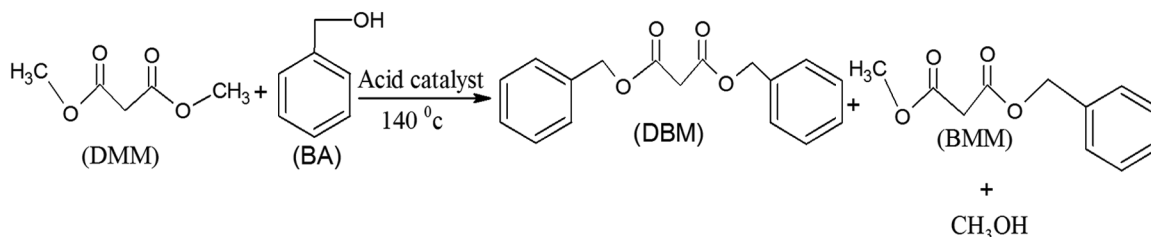
Preparation of sulphated ceria-zirconia ($\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$): 5.0 g of uncalcined hydrated mixed oxide $\text{CeO}_2\text{-ZrO}_2$ was taken in a china dish with a limited amount of deionized water to which 2 mL of 6M H_2SO_4 was added and the resulting mixture was made into a fine paste. The paste was dried at 120 °C for 12 h and calcined at 550 °C for 5 h.

Characterization of catalysts

All the catalysts were characterized for their surface acidity by NH_3 -TPD method. The crystallinity was analyzed by obtaining powder X-ray diffraction (PXRD) patterns recorded by X-ray powder diffractometer (Philips X'pert) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) over graphite crystal monochromator, The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet spectrometer in the range of 500–4000 cm^{-1} using KBr pellets.

Catalytic activity measurement

The activity of ceria, zirconia, ceria-zirconia, sulphated ceria and sulphated ceria-zirconia as catalytic material was determined in liquid phase transesterification of benzyl alcohol (BA) with dimethyl malonate (DMM). The reaction were carried out in a 50 mL two necked round bottomed flask fitted with water cooled condenser and thermometer packet on an oil bath with continuous stirring. Benzyl alcohol (5 mmol), dimethyl malonate (1 mmol) and 0.5 g of the solid acid catalyst were taken in a RB flask and the mixture was heated at 140 °C for 3 h (Scheme 1). After the reaction, the reaction mixture was cooled, filtered and the filtrate was analyzed by gas chromatography [Mayura analytical model 1110 and qualitatively analyzed by GC-MS (Varian)]. Column used for GC analysis of reaction products was 10% Carbowax column coupled with flame ionization detector. Typical GC operating conditions were FID temperature = 200 °C, Split flow = 100 mL/min, carrier gas = nitrogen at 1 mL/min. Temperature programming: 150 to 250 °C (at 10 °C min^{-1}).



Scheme 1 — Transesterification of dimethyl malonate with benzyl alcohol over a solid acid catalyst.

Selectivity of the reaction products were calculated using the formula:

$$\text{Product selectivity (\%)} = \frac{\text{GC peak area of the desired product}}{\text{GC peak area of DBM + BMM + MeOH}} \times 100$$

The reaction conditions were optimized by varying the parameters such as molar ratio of the reactants, reaction temperature, reaction time and weight of the catalyst. Kinetic parameters were determined by using the results obtained under optimization studies.

Results and Discussion

Total surface acidity (TSA)

The TSA values as well as acid site distribution of the solid acid catalysts are given in Supplementary Data, Table S1. The order of TSA values of solid acid catalysts are as follows:

$$\text{SCZ} > \text{SC} > \text{CZ} > \text{Z} > \text{C}$$

In comparison to solid acids, pure ceria was found to be least acidic. It has been reported that the addition of ceria into zirconia enhances the acidity of the resulting mixed oxide (i.e., CeO₂-ZrO₂) to a certain extent^{18,19}. The increase in acidity of solid acid catalyst may be explained as follows, the addition of zirconium cation into the ceria unit cell or vice versa changes the surface acid-base sites as the exposed Ce⁴⁺ and Zr⁴⁺ ions act as Lewis acid sites. Both CeO₂ and ZrO₂ exhibit the same metal-oxygen stoichiometry but possess different ionic characters. Ceria is considered to be more ionic than zirconia. Also, the acid strength of the mixed oxide varies depending on the charge-to-radius ratio of the cation. The Zr⁴⁺ ion has an ionic radius of 0.84 Å which is smaller than that of Ce⁴⁺ (0.97 Å) and is expected to generate a larger number of acid sites in their mixed form.

Literature survey shows that the sulfation of pure metal oxides increases the acidity to a reasonable extent²⁰. In the present study a similar finding has

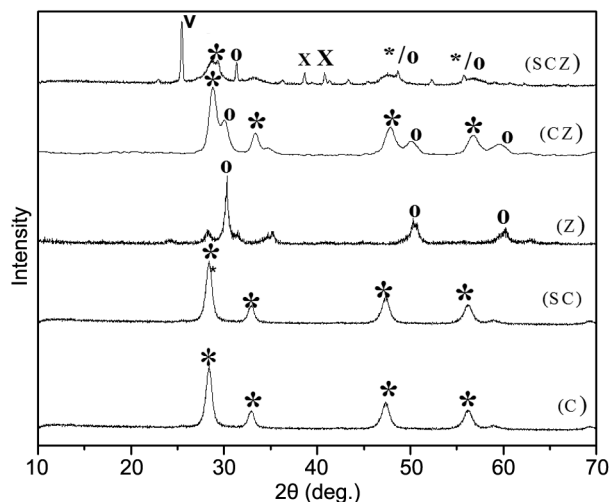


Fig. 1 — PXRD pattern of solid acids [* = ceria; o = tetragonal zirconia; v = Zr(SO₄)₂; x = Zr(OH)₂SO₄].

been observed. When compared to their pure forms, both SC and SCZ were found to be highly acidic. An increase in the surface acidity of SCZ, may be due to the existence of different types of sulphate phases such as CeOSO₄ and Zr(SO₄)₂ as reported by Putlasudarshan *et al*²¹. Further, it was observed that pure ceria or pure zirconia consisted of only 'weak' and 'moderate' acid sites. Whereas, CZ consisted of mostly 'moderate' acid sites. SC or SCZ consisted of 'moderate' as well as 'strong' acid sites.

PXRD analysis

PXRD patterns of the solid acids (C, Z, CZ, SC, and SCZ) are given in Fig. 1. Pure ceria shows fluorite structure with characteristic reflection at 2θ (deg.) = 28.5, 33.4, 47.3, 56.2²². Pure zirconia consisted of both monoclinic reflections at 2θ = 24.5, 28.3, 31, 41.5 and tetragonal reflections at 2θ = 30.2, 35.1, 50.4, 60.0. PXRD pattern of ceria-zirconia mixed oxide exhibit characteristic reflections of both fluorite structure of ceria as well as tetragonal phase of zirconia (2θ (deg.) = 30.2, 35.1, 50.4, 60.0)²³. However in ceria-zirconia, reflections due to monoclinic phase of zirconia were absent. This

indicates the structure stabilizing property of ceria on zirconia, wherein the tetragonal phase of zirconia is stabilized by ceria.

The effect of sulphate ion on ceria-zirconia could be observed via comparison of PXRD pattern of CZ and SCZ (Fig. 1). Reflections due to fluorite structure of ceria, tetragonal phase of zirconia and due to different types of surface zirconium sulphates such as zirconium sulphate hydroxide $[\text{Zr}(\text{OH})_2\text{SO}_4]$ and zirconium sulphate $[\text{Zr}(\text{SO}_4)_2]_4$ were observed in case of SCZ¹⁶. However no reflections pertaining to cerium sulphate were found in SCZ. Only ceria phases are observed in PXRD pattern of sulphated ceria²⁴.

FT-IR analysis

FT-IR spectra of ceria sample show a band at 1400 cm^{-1} which is Ce-OH stretching vibration in CeO_2 (Fig. 2). Bending and stretching vibrations of -OH group of water molecules present in the sample exhibit a peak at 1600 cm^{-1} and 3500 cm^{-1} ²⁵.

IR-Spectra of each sample show a peak at 3500 cm^{-1} which is due to hydroxyl group adsorbed on the surface of each solid acid catalyst which helps to generate Brønsted acidic sites. Similarly, all the above samples show a peak at 1600 cm^{-1} , due to the deformation mode of surface hydroxyl group. Each sample shows a band at $1110\text{--}1160\text{ cm}^{-1}$ in IR spectra which is due to M-O-M bonding. Appearance of band at 1118 cm^{-1} and $1400\text{--}1450\text{ cm}^{-1}$ in zirconia sample were assigned to Zr-O-Zr and Zr-OH stretching and bending modes respectively, confirming the formation of zirconia phase²⁶. In case of sulphated samples peak at

$1200\text{--}1300\text{ cm}^{-1}$ represents asymmetric stretching frequency of S=O double bond which is regarded as the characteristic peak of sulphate ion promoted super acids²⁷.

Catalytic activity studies

Transesterification reaction was carried out using different catalysts to obtain highest yield and the results are given in Supplementary Data, Fig. S1. The catalytic activity of solid acids are similar to their order of total surface acidity. i.e., $\text{SCZ} > \text{SC} > \text{CZ} > \text{Z} > \text{C}$. This indicates that total transester yield and TSA values are co-relative. Among the solid acid catalysts, pure ceria shows lowest activity for transesterification and sulphated ceria-zirconia shows highest activity for total transester product and also the formation of diester, this may be due to its high surface area. However, selectivity of the reaction product was found to be related to the acid strength of the catalytic material, since pure ceria, zirconia and ceria-zirconia consist of weak and moderate acidic sites, formation of monoester i.e., BMM is desirable. In case of SC and SCZ, formation of diester i.e., DBM is more favorable due the presence of moderate & strong acidic sites. Further, when the transesterification reactions were conducted in the absence of these catalytic materials, <8% yield of transester was observed indicating that the transesterification reactions are catalyzed reactions.

Effect of molar ratio of the reactants

Previous studies reported that to obtain high transester yield, excess amount of alcohol should be used²⁸. Molar ratio of DMM:BA (excess of BA) was changed from 1:1 to 1:7. The results are represented in Supplementary Data, Fig. S2a. When the molar ratio of DMM:BA was increased from 1:1 to 1:5 the yield of total transester increases. However selectivity of BMM decreases with an increase in the selectivity of DBM. The increase in the selectivity with increase in the molar ratio of DMM:BA may be because of the presence of more amounts of benzyl alcohol molecules in the reaction mixture. Further increase in the molar ratio beyond 1:5, results in the decrease in formation of total transester which may be due to the solvent effect of benzyl alcohol¹⁴.

Similarly, molar ratio of DMM:BA (excess of DMM) was studied in the range from 1:1 to 7:1 and the results are shown in the Supplementary Data, Fig. S2b. It was observed that when the concentration of DMM was increased, the total transester yield increases, however selectivity of BMM was found to

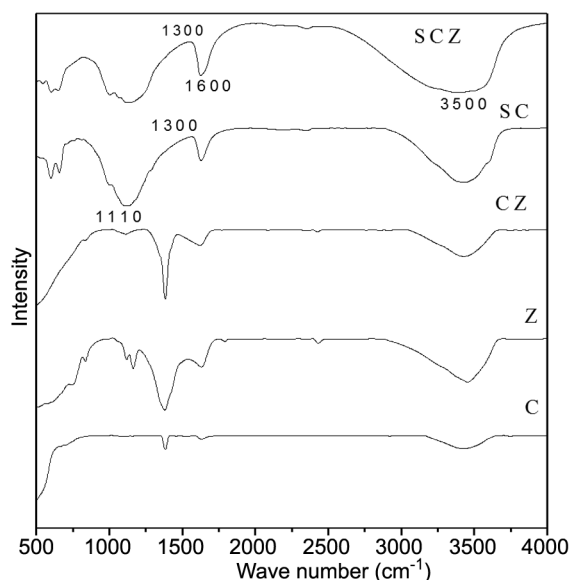


Fig. 2 — FT-IR spectra of studied solid acids.

increase with decrease in selectivity of DBM. In the present study increase in concentration of benzyl alcohol was more favorable to obtain high yield of required product. Hence for optimization molar ratio of 1:5 (excess of BA) was studied.

Effect of weight of the catalyst

The effect of loading of catalyst on transesterification reaction was studied by varying the amount of catalyst in the range 0.1 g to 0.7 g (Supplementary Data, Fig. S3). The percentage (%) yield of the product increases from 0.1 g weight of catalyst to 0.5 g and highest % yield of product was obtained when 0.5 g of catalyst was used in the reaction. On further increasing the weight of catalyst, the total transester yield decreases. Hence, for optimization 0.5 g of solid acid catalyst was selected for further studies.

Effect of temperature

The transesterification of DMM with BA was carried out in the temperature range 120 °C to 150 °C over SCZ catalyst to study the kinetics and optimize the reaction temperature (Supplementary Data, Fig. S4). The yield of the total transester and selectivity towards DBM increases with increase in the temperature up to 140 °C, which indicates that the formation of diester requires high temperature. Further increase in the temperature decreases the (%) yield of total transester, which might be due to the decomposition of reactant or product which leads to additional products other than the desired product. At high temperature, change in color of the reaction mixture to brown also supports this fact¹⁴.

Effect of reaction time

The total yield of transester product was studied against the reaction time by varying reaction time from 1 to 5 h over SCZ catalyst (Supplementary Data, Fig. S5). The total yield and selectivity towards DBM gradually increases with increase in the reaction time and reaches maximum at 3 h. After 3 h of reaction period, the total transester yield decreases but the selectivity towards DBM slightly increases while the selectivity towards BMM decreases. The formation of DBM for longer reaction periods can be attributed to the higher contact time between the reactants and the active sites of the catalytic material, which facilitates further reaction of the reaction intermediates to produce more DBM. Therefore, reaction time of 3 h was found to be

suitable for further optimization. A decrease in the yield of total transester after 3 h could be attributed to the formation of by-products other than BMM and DBM, when the contact time between the catalyst and the reactants or products was increased. Further, a slight change in the colour of the reaction mixture also supports this fact.

Kinetic study

Kinetic studies were conducted over ceria and its modified forms. Prior to the kinetic studies, experiments were carried out to establish the effect of mass transfer limitations of transesterification reaction. According to Madon and Boudart²⁹, a linear relationship exists between the rate of the reaction which indicates the absence of all transport limitations. Further, the effect of heat transfer limitation experiments were also conducted by varying different stirring rates of the reaction mixture and it was observed that there was no change in the yield of transester³⁰.

Plots of $-\ln[1-\text{yield}_{\text{Transester}}]$ versus reaction time for the transesterification were conducted at different temperatures over SC and SCZ catalyst (Supplementary Data, Fig. S6a and S6b). The plots are almost linear in all the cases, which indicate that the transesterification reaction was found to be a first order reaction. The values obtained from the slopes of the plots and the energy of activation calculated from the Arrhenius equation³¹ is presented in Supplementary Data, Table S2. The values of energy of activation of the catalyst for the transesterification were found to be in the order:

$$\text{SCZ} > \text{SC} > \text{CZ} > \text{Z} > \text{C}$$

Among the catalysts, SCZ shows lowest activation energy ($E_a = 29.93$ kJ/mol) value indicating that it could be a facile catalyst for the present work.

Effect of reusability of catalysts on the transesterification reaction

In order to study the reusability of solid acid catalyst, transesterification reaction of DMM with BA was carried with 0.5 g of SCZ at 140 °C for 3 h. The catalyst after the reaction was filtered, washed with acetone and dried at 120 °C for 2 h. Thereafter, it was calcined at 550 °C for 1 h and reused for transesterification reaction (Supplementary Data, Fig. S7a and S7b). There is no change in the total transester yield, selectivity towards both BMM and DBM over SCZ catalyst was observed. We can

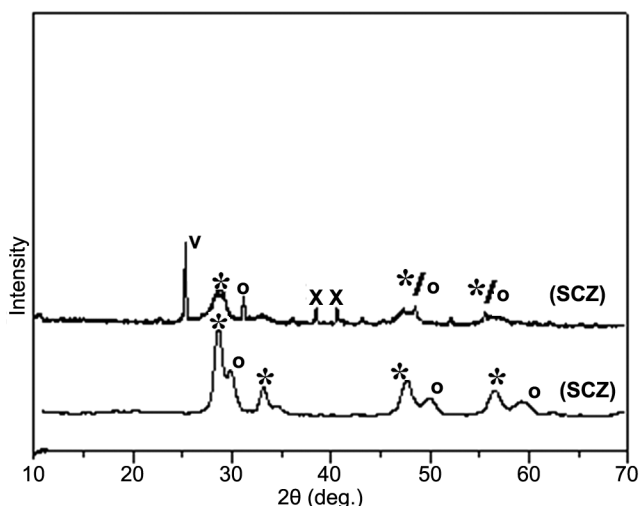


Fig. 3 — PXRD pattern of reused solid acid catalysts [* = ceria; o = tetragonal zirconia; v = $\text{Zr}(\text{SO}_4)_2$; x = $\text{Zr}(\text{OH})_2\text{SO}_4$].

conclude that without any appreciable loss in their catalytic activity, SCZ can be reactivated and reused up to 3 reaction cycles.

Characterisation of reused catalysts

The total surface acidity and PXRD analysis of reused catalysts are given in Supplementary Data, Table S3 and Fig. 3 respectively. There is not much change in the TSA values of freshly prepared catalyst and reused catalyst. The PXRD pattern of fresh catalyst and reused catalyst are nearly similar.

Leaching Studies

Leaching studies were conducted in order to show whether the reaction is homogeneously catalysed or not. In order to substantiate whether sulphate ions were leached out or not in the reaction medium, hot filtration experiments were performed. For hot filtration test, after 1 h of the reaction duration, the catalyst was removed by the filtration process. The filtrate obtained was subjected to transesterification reaction for further 2 h and then subjected to GC analysis (Supplementary Data, Fig. S8). In fact, there is no noticeable change in the conversion or selectivity of the product. The SCZ catalyst, which resists the leaching of sulphate ion species, clearly reveals its true heterogeneous nature. Hence, SCZ has better stability and well-isolated active sites and is a promising heterogeneous catalyst for transesterification reaction.

Conclusions

Ceria based solid acid catalyst SCZ was found to be an efficient catalytic material in the

transesterification reaction of DMM with BA. A correlation between the total surface acidity and the catalytic activity of the catalysts was observed. The solid acid catalyst SCZ, consisting of moderate and strong acid sites was found to be highly active in transesterification reaction of DMM with BA, with 96% selectivity of DBM. These solid acid catalysts are very efficient materials as they are easy to prepare, easy to use, easily removable, reactivable and reusable.

Supplementary Data

Supplementary data associated with the article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_57A\(11\)1344-1350_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(11)1344-1350_SupplData.pdf).

Acknowledgements

The authors are grateful for the financial support given by Vision Group of Science and Technology, Government of Karnataka (GRD-375/2014-15) India. The authors acknowledge PPISR Bangalore, India for PXRD analysis. The authors are thankful to Indian Institute of Technology- Madras, Chennai, India for TPD analysis and to University of Malaya, Kuala Lumpur, Malaysia for FT-IR analysis.

References

- 1 Manoj P, Zahira Y & Binitha N, *J Clust Sci*, 25 (2014) 1599.
- 2 Sunaja Devi K R & Jayashree S, *Reac Kinet Mech Cat*, 108 (2013) 183.
- 3 Sandip B R, Machhinndra K, Lande, R, Balasaheb, Arbad, Anil B & Gambhire, *Arabian J Chem*, 7 (2014) 253.
- 4 Mohammed Shamsuddin S Z & Nagaraju N, *J Chem Sci*, 122 (2010) 193.
- 5 Nagaraju N, Peeran, M & Prasad D, *React Catal Lett*, 6 (1997) 155.
- 6 Mohamed Shamsuddin S Z, Kurikose G & Nagaraju N, *Indian J Chem Technol*, 12 (2005) 447.
- 7 Zang X, He D H, Zhang Q J, Ye Q, Xu B Q & Zhu Q M, *Appl Catal A*, 81 (1999) 399.
- 8 Zang X, He D H, Zhang Q J, Ye Q, Xu B Q & Zhu Q M, *Appl Catal A*, 249 (2003) 107.
- 9 Mohamed Shamsuddin S Z, Shyamsundar M, Thimmaraju N, Venkatesh G, Vatsalya G & Senthilkumar M, *Comptes Rend Chim*, 15 (2012) 799.
- 10 Thimmaraju N, Pratap S R, Senthilkumar M & Mohamed Shamsuddin S Z, *J Korean Chem Soc*, 56 (2012) 563.
- 11 Pratap S R, Mohamed Shamsuddin S Z, Thimmaraju N & Venkatesh, *International J Chem Mol Nuc Mater Metall Eng*, 9 (2015) 1305.
- 12 Pratap S R, Mohamed Shamsuddin S Z, Thimmaraju N, Shyamsundar M & Reena S S, *Bangladesh J Sci Indus Res*, 50 (2015) 271.

- 13 Prasertthdam S, Wongmaneeenil P & Jongsomjit B, *J Ind Eng Chem*, 16 (2010) 935.
- 14 Thimmaraju N, Mohamed Shamshuddin S Z, Pratap S R & Venkatesh, *J Mol Catal*, 391 (2014) 55.
- 15 Vijayasankar A V, Mahadevaiah N, Bhat Y S & Nagaraju N, *J Porous Mater*, 18 (2011) 369.
- 16 Swarnali Pathak & Dibakar Chandra Deka, *Int J Sci & Eng Res*, 5 (2014) 1.
- 17 Minchitha, K U, Hareesh, H N, Venkatesh K, Shanty M, Nagaraju N & Kathyayini N, *J Nano sci and Nanotechnology*, 18 (2018) 202.
- 18 Pengpaniche S, Meeyoo V, Ricksomboon T & Bunyakiat K, *Appl Catal A*, 234 (2002) 221.
- 19 Reddy B M, Sreekanth P M , Lakshmanan P & Khan A, *J Mol Catal A*, 244 (2006) 1.
- 20 Sugunan S & Kumaree Seena C R, *Indian J Chem*, 38 A (1999) 1123.
- 21 Sudarsana P, Malleshm B, Reddy P S & Reddy B M, *J Chem Sci Technol*, 3 (2013) 161.
- 22 Sunaja Devi K R & Jayashree S, *React Kinet Mech Catal*, 108 (2013) 183.
- 23 Yadav G D & Nair J J, *Micropor Mesopor Mater*, 33 (1999) 1.
- 24 Rathod S, Navgire M, Arbad B & Lande M S, *Afr J Chem*, 65 (2012) 196.
- 25 Cimi Daniel A & Sugunan S, *Bull Chem React Eng Catal*, 8 (2013) 97.
- 26 Thimmaraju N, Mohamed Shamshuddin S Z, Pratap S R & Raja K, *RSC Adv*, 5 (2015) 99517.
- 27 Sunaja Devi K R & Jayashree S, *BCREC*, 7 (2013) 205.
- 28 Pallavi S, Ramaswamy V A, Lazar K & Ramaswamy V, *Appl Catal A*, 273 (2004) 239.
- 29 Madon R J & Boudart M, *Ind Eng Chem Fundam*, 21 (1982) 438.
- 30 Pratap S R, Mohamed Shamshuddin S Z & Mohan Kumar T E, *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 38 (2016) 3625.
- 31 Atkins P W, *Phys Chem*, (1988) 866.